Secretary).

PURPOSE: This book is intended for engineers and specialists in thermal power production, gas combustion, heat engineering and related fields.

COVERAGE: The collection contains three articles which deal with the combustion reaction rate and flame velocity in gaseous mixtures and the influence of ozone on the kinetics of hydrocarbon combustion. References appear at the end of each article.

TABLE OF CONTENTS:

reaction kinetics for mixtures of carbon monoxide with oxygen and nitrogen; Comparison of experimental data with calculated values of the total reaction rate of carbon monoxide with oxygen; On the conformity of exact and approximate solutions. The following personalities are mentioned: N. N. Semenov, D. A. Frank-Kamenetskiy, Ya.B. Zel'dovich, G. A. Barskiy, A. V. Bondarenko, N. A. Karzhvin, N. A. Karzhavina, L. S. Sclov'yeva, G. I. Kozlov, I. S. Bruk.

The author investigated the influence of ozone on critical conditions for the combustion of mixtures of some hydrocarbons with oxygen. Butane, Butylene and cyclohexane were investigated as it was possible to assume sustantial distinction in their primary interactions with ozone. The following personalities are mentioned: N. M. Chirkov, S. G. Entelis, A. B. Nalbandyan, B. Ya. Stern, N. A. Kleymanov, I. N. Antonova, A. M. Markevich.

Kinetics and Propagation of Flame (Cont.) SOV/2267

The influence of ozone on the burning velocity of butane was investigated at atmospheric pressure in air mixtures, and in oxygen mixtures at a pressure of 10 mm Hg.

AVAILABLE: Library of Congress

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IMS/mg
10-5-59

PSHEZHETSKIY, S.Ya.; KAMENETSKAYA, S.A.; GRIBOVA, Ye.I.; PANKRATOV, A.V.; MOROZOV, N.M.; POSPELOVA, I.N.; APIN, A.Ya.; SIRYATSKAYA, V.N.; SLAVINSKAYA, N.A.; CHERNEDNICHENKO, V.M.

Kinetics of the decomposition and explosion of ozone.
Probl.fiz.khim. no.2:27-38 '59. (MIRA 13:7)

1. Laboratoriya kinetiki gazovykh reaktsiy Nauchno-issledovatel'skogo fiziko-khimicheskogo instituta im. L.Ya.Karpova.
(Ozone) (Explosions)

PSHEZHETSKIY, S.Ya., professor

Effect of nuclear radiations on reactions in gases. Khim.nauka i prom. 4 no.4:509-515 '59. (MIRA 13:8)
(Radiation) (Gases)

5(4), 4(6) SOV/76-33-1-8/45

AUTHORS: Slavinskaya, N. A., Kamenetskaya, S. A., Pshezhetskiy, S. Ya.

TITLE: The Effect of Ozone on the Ignition of Hydrocarbons (Vliyaniye ozona na vosplameneniye uglevodorodov) II. Ignition of Butylene With Oxygen (II. Vosplameneniye butilena s kislorodom)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 1, pp 45-49 (USSR)

ABSTRACT: The effect of ozone (I) on the location of the ignition point and induction period of the ignition of a butylene (II)-oxygen (III) mixture was investigated and compared with the data regarding butane (Ref 1). (II) was obtained by the dehydration of n-butanol on aluminum oxide at 280-300°C, (I) and (III) as described in reference 1. Investgations were carried out with gas mixtures containing 80% (III) (from the stoichiometric amount) in a heatable vessel. The ignition point of (II) is somewhat lower than that of butane; the same applies to the induction period of the ignition. The data (Fig 2) were calculated from an equation found by N. N. Semenov. The values E = 42.2 kcal or 44 kcal were obtained for the activation energy. The effect of ozone is much stronger upon the ignition of (II) than upon that of butane. At a content of 2.5% (I) the

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The Effect of Ozone on the Ignition of Hydrocarbons. II. Ignition of Butylene With Oxygen

activation energy decreases to E = 8.85 kcal. This difference in the effect of (I) is explained by the primary reaction of (I) or of the atomic (III) with hydrocarbon at the double bonds, but not by the heat emission in the decomposition $O_3 \rightarrow 1.5\ O_2$. The dependence of the temperature on the pressure which was observed near the ignition point agrees with the theory of heat ignition. There are 6 figures, 1 table, and 2 references, 1 of which is Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moskva (Physico-Chemical Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED: May 31, 1957

SOV/76-33-2-5/45

5(4), 11(2)

AUTHORS: Slavinskaya, N. A., Kamenetskaya, S. A., Pshezhetskiy, S. Ya.

TITLE: The Effect of Ozone on the Ignition of Hydrocarbons (Vliyaniye ozona na vosplameneniye uglevodorodov). III. The Ignition of Cyclohexane With Oxygen (III. Vosplameneniye tsiklogeksana s kislorodom)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 2, pp 271 - 275 (USSR)

ABSTRACT: In continuing investigations previously reported (Refs 1,2) the primary reaction of ozone with cyclic hydrocarbons in the ignition of the latter was tested. The scheme used in the tests as well as the method for producing the ozone and oxygen has already been reported (Ref 1). A gas mixture was used which contained only 80% of the stoichiometric amount of oxygen. It was found that an addition of ozone lowered the ignition temperature (Fig 4) and the pressure threshold for ignition (Fig 5), while the induction period for ignition was avoided. Calculations for a gas mixture with 13.2% ozone show (Table 2) that the activation energy

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The Effect of Ozone on the Ignition of Hydrocarbons. III. The Ignition of Cyclohexane With Oxygen

SOV/76-33-2-5/45

lowered by the ozone from 43 kcal to 9.2 kcal. The effect of the ozone on the ignition of cyclohexane is similar to its effect on the ignition of butane, but less than in the case of the butylene ignition. The former is due to a similar primary reaction of butane and cyclohexane with ozone. The results obtained are in accord with the theory of heat ignition of N. N. Semenov and agree with the data obtained by N. A. Kleymenov, I. N. Antonova, A. M. Markevich, and A. B. Nalbandyan (Ref 3). There are 6 figures, 2 tables and 3 Soviet references.

ASSOCIATION: Akademiya nauk SSSR, Fiziko-khimicheskiy institut im. L. Ya. Karpova (Academy of Sciences, USSR, Physical-Chemical Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED: May 31, 1957

Card 2/2

5(4)
AUTHORS: Dmitriyev, M. T., Pshezhetskiy, S. Ya. SOV/76-33-2-36/45

TITLE: The Radiation Oxidation of Nitrogen (Radiatsionnoye okisleniye azota). IV. Temperature Dependence and the Part Played by Ions in the Reaction Under the Action of Fast Electrons (IV. Temperaturnaya zavisimost' i rol' ionov v reaktsii pod deystviyem bystrykh elektronov)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 2, pp 463-470 (USSR)

ABSTRACT: From the experimental results given in references 1 and 2 the reaction mechanism of the nitrogen oxidation at reduced pressure (1 mm Hg) can be explained in terms of the chemical reactions of the nitrogen ions. In the present paper the temperature function of the rate of reaction was investigated at a higher pressure (1 atm) and under the action of fast electrons with an energy of 200 kev. By removing the ions concerned from the reaction zone with a special probe the concentration of the positive and negative ions was varied. Data are given concerning the role of ion recombination and ion neutralization as well as several kinetic functions.

SOV/76-33-2-36/45

The Radiation Oxidation of Nitrogen.
IV. Temperature Dependence and the Part Played by Ions in the Reaction Under the Action of Fast Electrons

The energy of the electron beam was determined in a calorimeter with distilled water, while the nitrogen oxides were analyzed spectrophotometrically. The schematic representation of the testing apparatus is given (Fig 1). The following observations were made: the steady concentration of NO_2 is about 6%. The amount of NO_2 produced is proportional to the time the gas remains in the reaction zone and inversely proportional to the velocity of the penetrating radiation (Fig 2). The equation expressing the reaction rate (RG) as a function of the time is of second order (Table 2). The (RG) of the oxide decomposition is at constant conditions of 1 atm and 40° C about 50 times larger than the (RG) of the oxide formation. At concentrations below 2.5% NO_2 the NO_2 produced is proportional to the intensity of the irradiation (Table 3). With an increase in temperature the amount of NO_2 increases, reaching a maximum at about 200°C (Table 4). The values obtained for the activation energy lie between 1.2 and 1.7 kcal/mole.

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The Radiation Oxidation of Nitrogen. SOV/76-33-2-36/45
IV. Temperature Dependence and the Part Played by Ions in the Reaction Under the Action of Fast Electrons

The energy reaction yield at 1 atm and 15-20° for an air mixture is 1.3 - 1.5 molecules of NO_2 per 100 ev and increases with an increase in temperature to ca 200° to 3 - 3.5 molecules of NO_2 per 100 ev. The above mentioned experiments with special probes showed that the (RG) constant is proportional to the probability of the ionization of the nitrogen and that the conclusion of the previous paper is correct (Ref 2). The oxidation reaction is thus at the given conditions determined by the primary N_2 ionization and the secondary recombination processes of the ions. The coefficients of this temperature were determined as a function of the temperature. There are 3 figures, 5 tables, and 8 references, 6 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moskva (Physical-Chemical Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED: August 7, 1957

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05833
SOV/76-33-10-31/45

5(4)

AUTHORS: Pshezhetskiy, S. Ya., Morozov, N. M., Kamenetskaya, S. A., Siryatskaya, V. N., Gribova, Ye. I.

TITLE: Kinetics of the Thermal Decomposition of Ozone

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 10, pp 2306 - 2315 (USSR)

ABSTRACT: According to A. V. Pankratov and S. Ya. Pshezhetskiy (Ref 1), the quantum yield of photochemical ozone decomposition in liquid phase attains a value of 20. Investigations of the kinetics of thermal ozone decomposition have not fully explained this problem. Thus, values of 23-31 kcal were given for the activation energy in various publications. Further investigations of this problem were made by L.S. Kassel' (Ref 2), Benson, and Axworthy (Ref 3). In this article, the authors measured the reaction kinetics of thermal ozone decomposition at small, medium, and high ozone concentrations and various reaction surfaces within a wide temperature range. Experiments were made under static and dynamic conditions (at low concentration). The decomposition rate of ozone was determined at a pressure of 30-760 mm Hg and various initial ozone-hydrogen ratios within

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Kinetics of the Thermal Decomposition of Ozone

the temperature range 70-170°. The results of some typical experiments are listed (Tables 1-3). The velocity constant of decomposition, calculated according to the equation of second order, varies in dependence on the ratio $O_2:O_3$ as well as the "actual" activation energy which rises from 18 (95-97% O_3) up to 27 kcal (2-3% O_3). At very high and low ozone concentrations, the equation of second order holds with sufficient approximation. Extension of the reaction surface by 4.7 times does not change the reaction rate (Table 4). The factor before the exponent also varies with the composition of the gas mixture (Table 5). In concentrated mixtures, it is smaller by $10-10^2$ than the number of double collisions, and 10^2-10^4 times greater than the latter in dilute mixtures. An equation for the reaction rate was set up by the method of constant concentration which was suggested by Schumacher and Glissmann (Ref 10). The factors before the exponents and the activation energies were calculated for the four elementary reactions of the process (Table 6). The decomposition of ozone at the surface seems to be heterogeneous and of first order as confirmed by data by Markevich (Refs 6,7). There are 3 figures, 6 tables, and 24 references, 8 of which are Soviet.

05833

Kinetics of the Thermal Decomposition of Ozone SOV/76-33-10-31/45

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova, Moskva (Physicochemical Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED: March 31, 1958

Card 3/3

5(4)

AUTHORS: Dmitriyev, M. T., Pshezhetskiy, S. Ya. SOV/20-127-2-37/70

TITLE: Sensitization of Chemical Radiation Reaction by Means of an Ionic Charge Exchange

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 2, pp 369-372 (USSR)

ABSTRACT: Unlike photochemical sensitization which is based on the transfer of excitation energy, in chemical radiation reactions sensitization may take place by charge exchange on the collision of ions with molecules. This charge exchange makes it both possible to attain an increase in the concentration of chemically active ions as well as a suppression of unwanted chemical radiation processes. Sensitization by ionic charge exchange was investigated on the reaction of radiation oxidation of nitrogen by oxygen. The N_2^+ ion concentration was to be increased by the charge exchange of radiation-produced noble gas ions on the N-molecules. He, Ne and Ar were used. As their ionization potential lies above that of N, the following process was to occur: $N_2 + X^+ \longrightarrow N_2^+ + X$ (X = noble gas). Irradiation occurred

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with Co^{60}, absorbed γ-radiation was measured on the basis of the dosimetric oxidation of Fe^{II}. Exposure time amounted to 70 - 150 h, temperature 15 - 30°C, intensity of radiation 10^{13} - 5.10^{14} ev/cm^{2}sec. Investigation was extended to the zone of slight charge exchanges, in which there is still a linear dependence between the amount of oxidation products formed and adsorbed radiation energy (Fig 1), viz. no decomposition of reaction products occurs yet. Results are shown in figure 2. A part of the air was replaced by various amounts of inert gases. Despite sinking N- and O-contents, the reaction rate rises with rising content of inert gas. The effect of noble gases was investigated on the basis of the likelihood of an electron transition in nonelastic collision:

$\frac{a.\Delta E}{hv} \gg 1$ (a = constant of the magnitude of the gas kinetic collision radius, ΔE = variation of energy, h = Planck constant, v = relative velocity of colliding particles). Table 1 shows the computation results. For argon, the values agree with experimental data, for Ne and He the relative effect computed is inversely related to experimental data. The cause is assumed to

be a deviation of the distribution of positive ions from the Maxwell distribution, or the production of excited nitrogen ions in the reaction with Ne^+. A total coefficient β was computed for the effect of the charge exchange (Table 2). The effective cross section of the charge exchange may become for Ar $\sim$ 1 . When diluting the N-O mixture with noble gas, β drops, which fact may be caused by a recombination process concurring with the charge exchange: $X^+ + O_2 \longrightarrow \overrightarrow{X} + \overrightarrow{O_2}$. With high noble gas concentration, there may also occur a neutralization of noble gas ions at the vessel wall. Figure 3 shows the dependence of the energy yield on the composition of the gas mixture and on pressure. There are 3 figures, 2 tables, and 3 Soviet references.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

PRESENTED: March 5, 1959, by S. S. Medvedev, Academician

SUBMITTED: 28, 1959 (Abstracter's Note: no month given)

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77221
SOV/89-8-1-15/29

AUTHORS: Dmitriyev, M. D., Pshezhetskiy, S. Ya.

TITLE: Reactions of Nitrogen Dissolved in Water Induced by Ionizing Radiations. Letter to the Editor

PERIODICAL: Atomnaya energiya, 1960, Vol 8, Nr 1, pp 59-62 (USSR)

ABSTRACT: This communication contains some representative data about reactions of nitrogen with water and products of its radiolysis which the authors collected for the purpose of comparison with known data about the similar reaction of nitrogen with oxygen. These processes are important in nuclear engineering, and the authors were able on the bases of experimental data to investigate their probable mechanism. The theoretical findings will be the subject of the next communication. In the present experimental work Co^{60} γ-rays and fast electrons were used to oxidize the dissolved nitrogen into nitrate and nitrite and produce ammonia. 0.2 mev electrons were coming from an accelerator through a 15 μ thick aluminum

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foil and 1.5 cm of air and entering the container through an additional 10μ aluminum membrane. This membrane adhered closely to the liquid to prevent reactions with a possible gaseous phase. The absorbed electron energy was determined by means of a distilled water calorimeter comparing it to a constant current heater. The calorimeter sensitivity was $2 \cdot 10^{-2}$ degrees/min·watt. Gamma rays originated from 1.4 and 20 kcurie Co^{60} scurces. Exposures were performed in glass or stainless steel ampules. Gases were dissolved under pressure into bidistillates. During exposure the ion concentration was determined measuring electrical conductivity. After exposure the calorimetric determination of ions utilized the following reactions: disulphophenol acid and ammonia for the nitrate ion; α-naphthilamine and sulphanil acid for nitrite ion; mercuripotassium iodide in alkaline solution for the ammonia ion, reacting into mercuriammonium iodide. The lowest limit of these methods was

approximately 10^{-3} mgm. Figure 1 shows the relationship between the nitrate and nitrite yield and the absorbed radiation energy at different gas pressures.

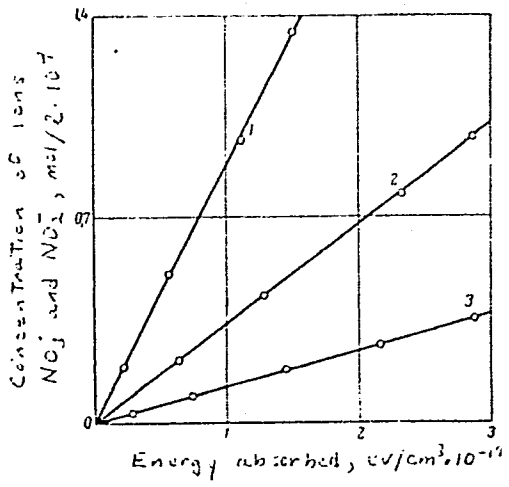

Fig. 1. Nitrate and nitrite concentration vs. absorption of radiation energy. Air pressure (in atmospheres): (1) 100; (2) 20; (3) 1.

The amount of bound nitrogen is proportional to the absorbed radiation energy up to 10^{19} or 10^{20} ev/cm^3. At higher values of absorbed energy the proportionality fails as seen on Fig. 2 whish represents data from fast electron exposures.

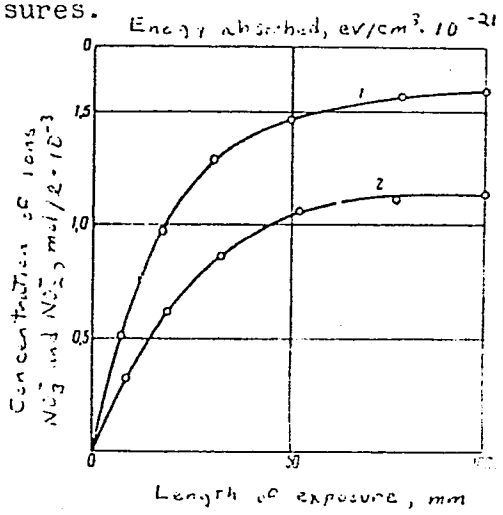

Fig. 2. Nitrate and nitrite ion concentration vs. exposure time to electrons of 200 kev (gas pressure 1 atm): (1) nitrogen; (2) air.

If during the experiment one supplies gas to the solution, the speed of the reaction remains constant, as seen in Table 1.

Table 1. Reaction speed versus length of exposure. (1 atm of air pressure over the solution, intensity of radiation $1.8 \cdot 10^{17}$ ev/cm^3·sec)

Length of exposure h	Nitrate and Nitrite Concentration 10^{-17} mol/cm^3	Reaction speed 10^{-14} mol/cm^3·sec	Speed constant of the first order 10^{-4} sec^{-1}
0,22	1,05	1,20	1,51
0,67	2,95	0,89	1,48
1,55	6,52	0,37	1,51
2,23	6,98	0,15	1,53
2,67	8,60	0,054	1,53
2,88	8,85	0,014	1,56

Consequently the energy yield is constant. One also sees from Fig. 3 the relationship between the reaction speed and pressure.

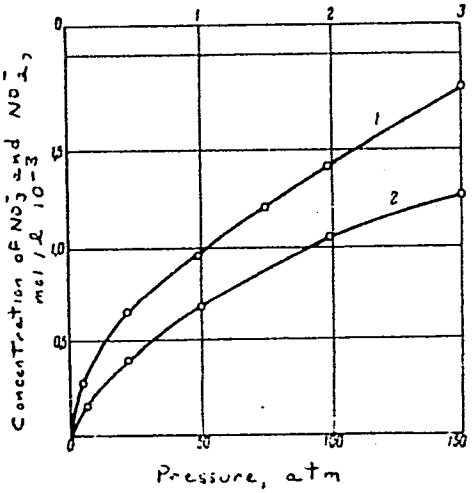

Fig. 3. Nitrate and nitrite concentration produced by γ-rays, vs. gas pressure. Radiation intensity $1.79 \cdot 10^{14}$ ev/sec·cm^3, 50 hours of exposure: (1) nitrogen; (2) air.

Table 2 gives the nitrite/nitrate ratio as function of absorbed energy, while Table 3 gives the ratio of ammonia to the sum of nitrate and nitrite.

Table 2. Nitrite to nitrate concentration ratio versus absorbed energy.

Absorbed energy, ev/cm³	Nitrite to nitrate concentration ratio			
	Nitrogen, atm			Air, 1 atm
	1	2	50	
10^{19}	3,3	2,7	1,5	0,7
10^{20}	1,8	1,5	0,9	0,4
10^{22}	0,5	0,4	0,3	0,1

Table 3. Ratio of ammonia and combined nitrate and nitrite ion yields versus absorbed energy.

Absorbed energy, ev/cm³	Relative yield of ammonia ions		
	Nitrogen, atm		Air, 1 atm
	1	100	
10^{18}	1,6	1,2	1,3
10^{20}	1,1	0,9	0,8
10^{22}	0,9	0,8	0,3

Further yields measured by the authors are given in Table 4 and 5.

Reactions of Nitrogen Dissolved in Water Induced by Ionizing Radiations. Letter on the Editor

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Table 4. Relative yield of nitrite and ammonia from nitrogen pressure (absorbed energy $2.2 \cdot 10^{19}$ ev/cm^3).

Pressure, atm	$[NO_2^-]/[NO_3^-]$	$[NH_4^+]/[NO_2^-]+[NO_3^-]$
1	3,3	1,55
10	2,8	1,52
50	1,5	1,35
100	1,2	1,22

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Table 5. Energy yield of reactions of nitrogen dissolved in water.

Pressure over the solution, atm	Composition of the gas, %	Nitrate yield, mol/100 ev	Nitrite yield, mol/100 ev	Ammonia yield, mol/100 ev	Yield of bound nitrogen atoms/100 ev
1	100 N_2	0,016	0,054	0,108	0,18
1	80 N_2+20 O_2	0,032	0,021	0,085	0,14
1	50 N_2+50 O_2	0,028	0,008	0,052	0,09
10	80 N_2+20 O_2	0,068	0,057	0,205	0,33
50	100 N_2	0,138	0,216	0,472	0,83
100	100 N_2	0,238	0,283	0,730	1,25
150	80 N_2+20 O_2	0,206	0,171	0,615	1,08
150	100 N_2	0,267	0,342	0,760	1,37

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There are 3 figures; 5 tables; and 9 references, 8 Soviet, 1 U.S. The U.S. reference is: J. Wright, J. Linacre, W. Marsh, T. Bates, Conference on the Peaceful Uses of Atomic Energy, Paper 445, Vol 7, New York, 1956, p 560.

SUBMITTED: January 6, 1959

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S 4300
S. 4500(B)

80230
S/076/60/034/04/30/042
B010/B009

AUTHORS: Dmitriyev, M. T., Pshezhetskiy, S. Ya. (Moscow)

TITLE: Radiation Oxidation of Nitrogen. V. The Kinetics of Nitrogen Oxidation Induced by γ-Rays and the Part Played by Ion Recombination Processes

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 4, pp. 880 - 887

TEXT: In earlier papers (Refs. 1,2) it has been observed that even at pressures below 1 atmosphere in the reaction kinetics of nitrogen oxidation induced by gamma radiation a considerable reduction of the constant of reaction rate is caused by the recombination processes of inversely charged ions. Since these processes depend to a great extent on pressure, the reaction kinetics was studied in the present paper within the range of pressure from 1 torr to 150 atmospheres at temperatures of from 15-25° and 150°. The gamma radiation of Co^{60} (1.4 and 20 kC) was used and the amount of energy absorbed was determined by means of the dosimetrical reaction of iron oxidation ($Fe^{2+} \rightarrow Fe^{3+}$). The measured values show that the amount of NO_2 obtained is proportional to the duration and intensity of

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80230

Radiation Oxidation of Nitrogen. V. The Kinetics of Nitrogen Oxidation Induced by γ-Rays and the Part Played by Ion Recombination Processes

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B010/B009

irradiation. The ratio N_2O : NO_2 increases with increasing pressure. The N_2O yield is as little as 1/2 to 1/3 of the NO_2 yield. The pressure increase up to 1 atmosphere causes the energy yield to drop, at pressures above 1 atmosphere the yield increases to reach a value of 5-6 molecules of NO_2 per 100 ev at 150 atmospheres (Table 1). The dependence of the reaction rate upon the composition of the reaction mixture corresponds to an equation of the second order, while the dependence of both the reaction rate and energy yield on pressure deviates from this equation. This deviation is held to be due to the ion recombination. Tables 2 and 3 contain the values of the dependence of the recombination coefficient upon pressure. Data concerning the relation between the constant of the reaction rate and the coefficients of ion recombination are also given. The authors conclude by thanking Ye. I. Zolotarev, Ye. V. Bol'shun, Z. I. Vyazovikina, and F. M. Rappoport for their assistance with the measurements. There are 6 figures, 3 tables, and 11 references, 7 of which are Soviet.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova Moskva (Physico-chemical Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED: July 9, 1958

Card 2/2

Pshezhetskiy, S. Ya.

3

S/076/60/034/05/05/038
B010/B002

AUTHORS: [illegible], N. A., Kaschevich, V. Ya., Kazenetskaya, S. A., [illegible], V. N., Pshezhetskiy, S. Ya.

TITLE: The Burning Rate of Ozone - Oxygen Gas Mixtures

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 5, pp. 973-978

ABSTRACT: The authors wanted to find out whether there is a relationship between the rate of the slow decomposition and the burning rate of ozone. For this purpose, they measured the propagation velocity of the flame in mixtures of ozone with oxygen in a horizontal glass tube. The photoelectric method served for determining the flame passage, and a multiple device was worked out (Fig. 1). The flame front area was recorded photographically with a movie camera. The results obtained are tabulated, and are compared (Fig. 2) with the results obtained by P. Laffitte (Ref. 3) and A. G. Strang and A. V. Grosse (Ref. 4). A good agreement is found among them. Experimental data obtained for the dependence of the burning rate on the gas mixture composition, are in

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good agreement with the values calculated from the Zel'dovich-Frank-Kamenetskiy-Semenov equation (Ref. 7). The calculated absolute values are smaller than the experimental ones. A comparison between data given here and those from Ref. 4 and the paper by T. Karman (Ref. 5) revealed that the burning rate of ozone in oxygen mixtures corresponds to the reaction kinetics of thermal ozone decomposition. N. N. Semenov is mentioned in the text. There are 2 figures, 1 table, and 11 references: 4 Soviet, 6 American, and 1 German.

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ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Institute of Physical Chemistry imeni L. Ya. Karpov)

SUBMITTED: May 25, 1958

Card 2/2

81564

S/076/60/034/06/03/040
B015/B061

11.1000
5.4500B

AUTHORS: Slavinskaya, N. A., Kamenetskaya, S. A., Pshezhetskiy, S. Ya., Vasil'yev, L. A. (Moscow)

TITLE: The Influence of Ionizing Radiation on the Kinetics of the Oxidation and Ignition of Butane. I. Formal Kinetics

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 6, pp. 1169-1175

TEXT: The influence of fast electrons and of a static discharge on the formal kinetics of the chain reaction of butane oxidation with oxygen was examined. An electron accelerator was used, and the pressure in the reaction vessel was changed from 582 to 640 torr, and the temperature from 40 to 254°C. The strength of the discharge current was measured with an МВЛ-2М (MVL-2M) cathode voltmeter. It was established that irradiation with fast electrons accelerated the butane oxidation and decreased the induction period and the effective activating energy. The latter falls from 45 to 15 kcal/mole with an increase in the radiation intensity. The effect of radiation on the reaction kinetics is mainly due to the

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The Influence of Ionizing Radiation on [illegible] Kinetics of the Oxidation and Ignition of Butane. I. Formal Kinetics

S/076/60/034/06/03/040 (81564)
B015/B061

formation of primary active centers of the chain reaction in the ionization and excitation of the molecules, and to the reactions of atomic oxygen with carbon. On the basis of N. N. Semenov's theory of branched chain reactions, the results of the tests were analyzed, and agreement with the theory was established (Table 1, data on the rate of formation of active centers and chain reactions; Table 2, values of the effective activating energy). Tests on the ignition of butane with oxygen in a vessel heated to 520°C showed that radiation shortens the induction period of the ignition of the mixture, and that the character of the dependence corresponds to that of the effect of radiation on the kinetics of the oxidation. N. M. Emanuel' is mentioned in the text. There are 6 figures, 2 tables, and 4 Soviet references.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova Moskva
(Physicochemical Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED: May 25, 1958

Card 2/2

PSHEZHETSKIY, S.YA.

11.5000

81970
S/076/60/034/07/01/009
B015/B070

AUTHORS: Gribova, Ye. I., Kamenetskaya, S. A., Pankratov, A. V., Apin, A. Ya., Pshezhetskiy, S. Ya.

TITLE: The Critical Diameter and the Explosion Rate of Liquid Ozone Solutions

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 7, pp. 1395-1401

TEXT: According to the theory of Yu. B. Khariton (Ref. 1) the critical diameter of an explosive is the minimum diameter of a cylindrical charge in which a stable detonation at a constant rate may occur. The critical diameter of the explosive is proportional to the duration of the reaction in the front of the explosive wave and this duration is inversely proportional to the reaction rate. In the present work the dependence of the critical diameter on the composition of the liquid ozone sample diluted with oxygen or carbon tetrafluoride is investigated. The experimental apparatus is shown schematically in Fig. 1. The explosion was started by lead azide in a suitable apparatus (Fig. 2), and for experiments with

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(3)

81970

The Critical Diameter and the Explosion Rate of Liquid Ozone Solutions

S/076/60/034/07/01/009
B015/B070

oxygen - ozone mixtures the gaseous mixture was condensed in a receiver (Fig. 3). The measured values (Table 1, oxygen - ozone mixtures with 37-40% O_3; Table 2, 47% O_3; Table 3, 32-95% O_3; Table 4, experiments in small brass tubes with heterogeneous mixtures; Table 5, CF_4-O_3 mixtures) show that the explosion properties of ozone are determined principally by the character of the kinetics of decomposition, i.e., by the small activation energy and the large factor of the exponential function. The relation obtained between the critical diameter and the composition of the solutions agrees with the above-mentioned theory of the critical diameter of stable detonations. Measurements on the rate of explosion of an ozone - oxygen mixture with 96% ozone (Table 6) showed that the rate of detonation is not proportional to the ozone concentration. A. F. Belyayev is mentioned in the text. There are 5 figures, 6 tables, and 6 Soviet references.

ASSOCIATION: Fiziko-khimicheskiy in-t im. L. Ya. Karpova (Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: February 22, 1958

Card 2/2

POLUEKTOV, V.A. (Moscow); PSHEZHETSKIY, S.Ya. (Moscow); CHEREDNICHENKO, V.M. (Moscow)

Critical conditions for the inflammation of butane with oxygen and the effect of surface. Zhur. fiz. khim. 35 no.2:389-392 F '61. (MIRA 16:7)

1. Fiziko-khimicheskiy institut imeni Karpova.
(Butane) (Combustion)

5.4600
26.2312

24019
S/076/61/035/005/002/008
B101/B218

AUTHORS: Dmitriyev, M. T. and Pshezhetskiy, S. Ya. (Moscow)

TITLE: Radiation oxidation of nitrogen. VI. Sensitization of the oxidation of nitrogen by charge exchange between the nitrogen molecule and ions of inert gases

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 5, 1961, 1010-1018

TEXT: In previous papers (Ref. 1: Sb. "Deystviye ioniziruyushchikh izlucheniy na neorganicheskiye i organicheskiye sistemy (Effect of ionizing radiation on inorganic and organic systems), Izd-vo AN SSSR, M. 1958, p. 145; Ref. 2: Zh. fiz. khimii, 32. 2418, 1958) it was found that oxidation of nitrogen is caused by ionization of N_2 molecules and may be accelerated by increasing the concentration of N_2 ions. Such an increase in concentration can be brought about by transferring an electron from the N_2 molecule to positive inert-gas ions: $N_2 + X^+ \rightarrow N_2^+ + X$ (1). The authors studied the sensitization of radiation oxidation of N_2 by means

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Radiation oxidation of nitrogen. ...

of reaction 1. Some data have already been published (Ref. 3: Dokl. AN SSSR, 127, 369, 1959). The method is described in Refs. 1, 5, and 6 (Ref. 5: Zh. fiz. khimii 33, 463, 1959; Ref. 6: ibid., 34, 880, 1960). Two series of tests were performed: a) mixtures of N_2 and He were irradiated at 1-150 atm above a water surface; b) the oxidation rate of N_2 in $N_2 + O_2$ mixtures was studied as a function of the absorbed energy, of pressure, and of the composition of the mixtures, both in the presence of He at 0-150 atm, and in the presence of Ne and Ar at 1 atm. A linear relation between the formed NO_2 and the absorbed energy was found for mixtures of air and He, Ne or Ar. Fig. 2 represents the reaction rate as a function of pressure up to 1 atm; Fig. 4 shows the same as a function of composition if part of the mixture $N_2 + O_2$ is replaced by inert gases. If the latter had no effect, the reaction rate would follow the dashed lines. Table 2 gives some typical energy yields. Ionization and charge exchange in mixtures of N_2 + inert gas are given as: $N_2 \xrightarrow{k_1} N_2^+ + e$ (3);

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Radiation oxidation of nitrogen...

$X \xrightarrow{k_2} X^+ + e$ (4); $X^+ + N_2 \xrightarrow{k_3} N_2^+ + X$ (5); $[X]^+ = (k_2/k_3)[X]/[N_2]$ (6); the formation rate of N_2^+ ions is given by: $d[N_2^+]/dt = k_1([N_2] + \beta[X])$ (7), where $\beta = k_2/k_1$. Table 3 shows values of β as calculated from Eq. (7). In the presence of O_2, also recombinations of ions: $X^+ + O_2^- \longrightarrow X + O_2$ (2) may occur. Besides, the following reactions may take place: $N_2^+ + O_2 \xrightarrow{k_4} N_2 + O_2^+$ (9); $O_2 + e \xrightarrow{k_5} O_2^-$ (10); $N_2^+ + O_2^- \xrightarrow{\alpha} N_2 + O_2$ (11); $X^+ + O_2^- \xrightarrow{k_6} X + O_2$ (12); $N_2^+ + O_2 \xrightarrow{k_7} NO^+ + NO$ (13). One obtains: $v = k_7([N_2] + \beta'[X])[O_2]$ (19), where $\beta' = (k_3/k_2)(k_1 + k_2[X]/[N_2])[N_2]/[X]$ (20). β' decreases with increasing concentration of the inert gas (Table 4), which is caused by the recombination process 2. It may also be seen from Table 4 that the recombination coefficient α is strongly reduced if the pressure rises. The sensitizing effect of the inert gases is due to the ratio He:Ne:Ar=1:1:16:1:40. The action of the inert gases is due to their charge transfer in collisions

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Radiation oxidation of nitrogen...

with the N_2 molecule. There are 6 figures, 6 tables, and 6 Soviet-bloc references.

ASSOCIATION: Institut im. Karpova, Moskva (Institute imeni Karpov, Moscow)

SUBMITTED: June 26, 1959

Fig. 2: Reaction rate as a function of pressure. Exposure 112 hr. Maximum intensity of irradiation $1.6 \cdot 10^{14}$ ev/cm^3. Temperature 21°C. Capacity of the ampoule 30 cm^3. Legend: a) initial air pressure 200 mm Hg; б) 70 mm Hg; 1) air; 2) argon; 3) neon; 4) helium; x) pressure, mm Hg; y) reaction rate, molecules/cm^3·sec.

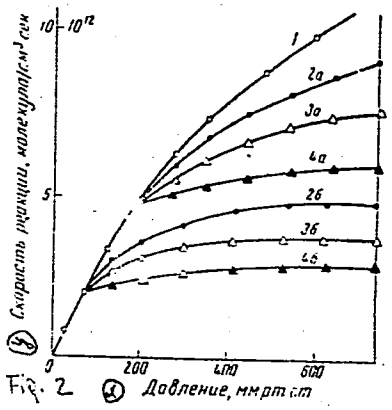

Fig. 2

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28294 S/076/61/035/010/013/015
B106/B110

11.6100

AUTHORS: Yermakova, S. K., Cherednichenko, V. M., and Pshezhetskiy, S. Ya.

TITLE: Reaction kinetics and inflammation of nitrogen dioxide with n-butane

PERIODICAL: Zhurnal fizicheskoy khimii, v. 35, no. 10, 1961, 2352-2357

TEXT: The authors studied the reaction kinetics and the inflammation in the system NO_2 - n-butane, since the kinetics of reactions of NO_2 with higher hydrocarbons had not yet been studied. Fig. 1 shows the experimental arrangement used. The measurements were carried out statically. The reaction rates were measured both photometrically on the basis of the decrease in NO_2 concentration, and on the basis of pressure changes in the system. The kinetic measurements were made at temperatures of 250 - 450°C and pressures of 8-35 mm Hg, and the limits of inflammation were determined at 375 - 525°C and 20 - 170 mm Hg. The reaction of NO_2 with n-butane was found to be of the order of 0.7 with respect to butane, which resulted

Card 1/6

from the dependence of the reaction rate on the partial pressure of butane at 300°C. The order with respect to NO_2 is approximately 1.4. The over-all reaction order is about 2.1, and does not change even on transition to temperatures of 400 - 450°C. When measuring the temperature dependence of the reaction rate, an MPO-2 (MPO-2) galvanometer oscilloscope had to be used at 400 - 450°C for measuring the photocurrent, as the high reaction rate did not permit a visual measurement in the initial stage of the reaction. Fig. 4 shows the temperature dependence of the reaction rate. From the ascent of the straight line in this diagram, the activation energy of the reaction was determined to be 30 kcal/mole. Therefore, one obtains the following kinetic equation for the reaction of NO_2 with n-butane: $w = k_0 \exp(-3.0 \cdot 10^4/RT)(C_4H_{10})^{0.7}(NO_2)^{1.4}$ (1). A particular feature of the reaction studied is the monotone increase in pressure during the reaction. It is assumed nowadays that the primary event of the reaction is the formation of a radical: $C_4H_{10} + NO_2 = C_4H_9^{\cdot} + HNO_2$; ($\Delta H \approx 14$ kcal/mole) (2). Subsequently, either a nitroalkane or an alkyl nitrite is formed from this radical with NO_2. Both possibilities are

almost equally probable (Ref. 6: T. V. Fedorova, A. P. Ballod, A. V. Topchiyev i V. Ya. Shtern, Dokl. AN SSSR, 123, No. 5, 1958). The thermal stabilities of nitroalkanes and alkyl nitrites differ very much, as the decomposition of the former is characterized by much higher activation energies (39 - 53 kcal/mole) and lower values of the pre-exponential factor than the decomposition of the latter (36-38 cal/mole, $1.8 \cdot 10^{13} - 3 \cdot 10^{14}$)(Ref. 11: see below). Under the present experimental conditions, nitroalkanes accumulate in the initial stages of the reaction, while the alkyl nitrites decompose to form gaseous products. This is probably the cause of the pressure increase from the beginning of the process. Fig. 5 illustrates the measurement of the inflammation limits for mixtures of the composition $C_4H_{10} + 6.5\ NO_2$. Assuming that the inflammation be a thermal explosion, the effective activation energy of the reaction which gives rise to inflammation was calculated to be 28 kcal/mole. This value is close to that obtained for the slow reaction of NO_2 with n-butane (30 kcal/mole). This fact and the above-mentioned constancy of the over-all reaction order with an increase in temperature suggest that the critical conditions of inflammation obey the kinetic laws of the slow

reaction. Two papers by A. B. Gagarina and N. M. Emanuel' are mentioned (Ref. 7: Zh. fiz. khimii, 33, 1641, 1959; Ref. 8: Zh. fiz. khimii, 33, 1872, 1959). There are 5 figures, 3 tables, and 12 references: 7 Soviet and 5 non-Soviet. The three most important references to English-language publications read as follows: W. A. Rosser, H. Wise, J. Chem. Phys., 26, 571, 1957; Ref. 11: E. W. R. Steacie, Atomic and free radical reactions, N. Y., 1956; P. Gray, Proc. Roy. Soc., A221, 462, 1954.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

SUBMITTED: March 4, 1960

5.4600
11.1320

24060
S/020/61/138/004/021/023
B103/B203

AUTHORS: Sorokin, Yu. A. and Pshezhetskiy, S. Ya.

TITLE: Formation of hydrazine under the action of γ-radiation on ammonia in liquid and solid state

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 138, no. 4, 1961, 880-883

TEXT: The authors studied the formation of hydrazine N_2H_4 in liquid and solid ammonia under the action of γ-rays. Ammonia was treated in quartz ampuls with γ-rays of Co^{60} with an activity of $2 \cdot 10^4$ curie for $10\text{-}10^4$ min. The radiation intensity was varied between 25 and 790 r/sec. Ammonia was removed by evaporation after irradiation. N_2H_4 was determined photocolorimetrically in hydrochloric acid solution of p-dimethyl-amino benzaldehyde. In the liquid phase, the N_2H_4 yield increases with decreasing temperature. It decreases, however, abruptly by one order of magnitude after overstepping the coagulation point of ammonia (-78°C). The temperature dependence of the N_2H_4 yield in the liquid phase corresponds

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Formation of hydrazine under the action ...

to an activation energy of 3—4 kcal/mole. The authors explain the above-mentioned influence of the phase condition with a change of formation conditions of NH_2 radicals. According to their opinion, the following essential reactions lead to the formation of N_2H_4: (1) $NH_3 \rightleftarrows \begin{cases} NH_2+H \\ NH+H_2 \end{cases}$; (2) $NH_2 + NH_2 \longrightarrow N_2H_4$; (3) $NH + NH_3 \longrightarrow N_2H_4$. The concentration of NH_2 radicals depends on the recombination of hydrogen atoms (H) with their initial NH_2 radical. The withdrawal of an H atom from the initial NH_2 radical is easier in the liquid than in the solid phase. Therefore, any acceptor of H atoms should increase the N_2H_4 yield. The acceptor should be more efficient in the solid phase. Propylene was used as acceptor. To eliminate, as far as possible, the distortion of the solid ammonia lattice by the acceptor molecules, the authors made parallel tests with propane which is no acceptor for H atoms. The N_2H_4 yield in solid ammonia was shown to increase with increasing amount of propylene. Equal amounts of propane had no effect. In liquid ammonia, the N_2H_4 yield did not rise

Formation of hydrazine under the action ...

with the addition of propylene. Although this confirms the assumption of the effect of a recombination of H atoms with the NH_2 radicals, other effects are likely to participate such as the difference in recombination conditions of NH_2 radicals on formation of N_2H_4 (as well as of the reaction of NH radicals with NH_3 molecules). The liquid phase favors both the formation of $\dot{N}H_2$ radicals and their interaction. In the solid phase, there is no such mobility, and recombination of the $\dot{N}H_2$ radicals, or of NH with NH_3, hardly occurs. These reactions are not favored by low temperatures either, as was confirmed by the electron paramagnetic resonance. The results obtained suggest that there is practically no reaction in the solid phase. It appears that the reaction starts during the thawing of irradiated specimens when the particles have regained a certain mobility. The negative temperature dependence of the N_2H_4 formation in liquid ammonia may depend on: (1) N_2H_4 decomposition. Since with low N_2H_4 concentrations negligible amounts of radiation are absorbed by its molecules as compared

Formation of hydrazine under the action ...

with those of ammonia, the N_2H_4 decomposition should be mainly due to the interaction with, for instance, NH_2 or NH radicals. Such reactions are accelerated with rising temperature, which must lead to a decrease in the N_2H_4 content. The cooperation of the formation reactions of N_2H_4 (reaction 2, for instance) with the above-mentioned decomposition reactions leads to a nonlinear dependence of the N_2H_4 concentration on the energy dose so that the N_2H_4 concentration must attain steady values in the case of sufficiently high energy doses. Experimental data, however, show no deviations from linearity in the range of the doses used. (2) Acceleration of diffusion of NH_2 radicals from the tracks with rising temperature, thus making recombination and N_2H_4 formation less probable. This mechanism corresponds to the value of the negative activation energy in an order of magnitude of 3 — 4 kcal/mole. The authors' N_2H_4 yields of about 0.2 molecules/ev correspond to the value determined in Ref. 1 (Ye. V. Bol'shun, S. Ya. Pshezhetskiy, I.A.Myasni[illegible]v, Sborn. Deystviye

Card 4/5

24060
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B103/B203

Formation of hydrazine under the action ...

ioniziruyushchikh izlucheniy na neorganicheskiye i organicheskiye sistemy (Effect of ionizing radiation on inorganic and organic systems), Izd.AN SSSR, 1958, p.184) on irradiation of liquid ammonia with fast neutrons (about 0.7 molecules/100 ev). There are 4 figures, 1 table, and 1 Soviet-bloc reference.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-chemical Institute imeni L. Ya. Karpov)

PRESENTED: January 20, 1961, by S. S. Medvedev, Academician

SUBMITTED: October 20, 1960

Card 5/5

PHASE I BOOK EXPLOITATION SOV/6318

Pshezhetskiy, Samuil Yakovlevich

Mekhanizm radiatsionno-khimicheskikh reaktsiy (The Mechanism of Radiation Chemical Reactions). Moscow, Goskhimizdat, 1962. 306 p. Errata slip inserted. 4000 copies printed.

Ed.: Ts. I. Zalkind; Tech. Ed.: V. F. Zazul'skaya.

PURPOSE: This book is intended for scientists, chemical engineers, and graduate students as an introduction to radiation chemistry.

COVERAGE: The book reviews progress in radiation chemistry through 1962, chiefly on the basis of non-Soviet literature. The text is concerned primarily with gaseous reactions and to a lesser degree with reactions in condensed phases. Polymerization and conversions of polymers are discussed only briefly. The author thanks V. L. Tal'roze for reviewing the manuscript. Soviet and non-Soviet references are given at the end of each chapter.

Card 1/3

43232
S/844/62/000/000/047/129
D287/D307

AUTHORS: Sorokin, Yu. A. and Pshezhetskiy, S. Ya.

TITLE: The formation of hydrazine during γ irradiation of solid and liquid ammonia

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 279-281

TEXT: The effect of the state of phase on radiolytic processes was investigated in the case of hydrazine, which was prepared by irradiating liquid and solid ammonia. Experiments to establish the relationship between the yield of hydrazine and temperature during irradiation indicated that the yields increased with decreasing temperatures of liquid NH_3, but decreased sharply on reaching the freezing point of ammonia and were lower in the solid state (by approximately one order of magnitude). This temperature dependence in the liquid state is assumed to be due to decomposition of hydrazine. The required activation energy was 3 - 4 kcal/mole. The observed

Card 1/2

S/844/62/000/000/059/129
D204/D307

AUTHORS: Slavinskaya, N. A., Kamenetskaya, S. A., Pshezhetskiy, S. Ya. and Zhitneva, G. P.

TITLE: A study of the kinetics of the chain oxidation of butane in the vapor phase, under the action of fast electrons

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 353-356

TEXT: Kinetics of the aerial oxidation of gaseous butane were studied under steady irradiation with fast electrons (the energy absorbed by the gas ρ being 0.6, 1.2 or 2.4 x 10^{16} ev/cm^3.sec) at 613 - 640 mm Hg and between 185 and 257°C, to elucidate the mechanism of such reactions. The intermediate oxidation products were estimated polarographically, the unchanged butane chromatographically, and the reaction rate was followed by the increase in pressure, Δp. The log Δp/time plots were linear in all cases, as predicted by the kinetic equations derived for branched-chain mecha-

nisms by N. N. Semenov. Both the initial number of active centers, n_0, and a parameter characterizing the extent of chain-branching increased linearly with increasing intensity of irradiation, whilst the effective activation energy was decreased. A mathematical treatment is presented, showing that the rates of oxidation of hydrocarbons under constant irradiation may be described by branched-chain kinetic equations, the actual parameters being a function of the irradiation intensity. The relative increase in n_0 under the action of irradiation was comparatively lower at higher temperatures. The effect of radiation on chain-branching is ascribed to the action of the irradiation on intermediate oxidation products (aldehydes and peroxides); these products were shown to decompose in proportion to the duration of irradiation. There are 5 figures.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-Chemical Institute im. L. Ya. Karpov)

30429
S/076/62/036/006/003/011
B117/B138

5.4600

AUTHORS: Slavinskaya, N. A., Zhitneva, G. P., Kamenetskaya, S. A., and Pshezhetskiy, S. Ya.

TITLE: Effect of ionizing radiation on the kinetics of butane oxidation. II. Reaction mechanism

PERIODICAL: Zhurnal fizicheskoy khimii, v. 36, no. 6, 1962, 1293 - 1298

TEXT: The first section of this report (I) (N. A. Slavinskaya, S. A. Kamenetskaya, S. Ya. Pshezhetskiy, L. A. Vasil'yev, Zh. fiz. khimii, 34, 1169, 1960) dealt with the formal kinetics of chain reactions in butane oxygen oxidation. This section describes studies of the oxidation mechanism of butane under fast electron irradiation with particular attention to its effect on the ramification of the reaction chain. The source was an electron accelerator with extracted beam of three intensities 25, 50, and 100 μa. The electron energy absorbed by the gas was determined from the decomposition of nitrogen oxide: 0.6 at 25 μa, 1.2 at 50 μa, and $2.4 \cdot 10^{15}$ ev/cm^3 at 100 μa. The reaction rate was measured by the method des-

Card 1/3

cribed in I. Besides the chromatographic determination of butane, also the products of its partial oxidation (peroxides and aldehydes) were also studied polarographically. Experimental conditions: initial pressure of the butane - air mixture = 613 mm Hg; temperature = 185 - 257°C. The temperature dependence of the reaction rate was recorded at two radiation intensities ($1.2 \cdot 10^{15}$ and $2.4 \cdot 10^{11}$ ev/cm^3.sec). As in I, the main parameters of the reaction kinetics were determined from experimental curves, using the equations suggested by N. I. Semenov (O nekotorykh problemakh khimicheskoy kinetiki (Some problems of chemical kinetics) Izd-vo AN SSSR, 1954) for ramified chain reactions. It was found that the effective activation energy E_{eff} decreased and the number of initial active centers n_o and the ramification factor γ increase as radiation intensity rose. This is consistent with the previously determined dependence of these parameters on the intensity of the electron beam. Accelerated accumulation of peroxides and aldehydes was found with rising intensity of the electron beam. Examination of their concentration as a function of this intensity showed that they decompose under the action of electrons. The amount of decomposing peroxides was proportional to the radiation intensity. The

Effect of ionizing ...

decomposition of aldehydes is more complicated, and they are assumed to play a less significant part in chain ramification. Summary: The greater ramification of the chain at high radiation intensity cannot only be due to the formation of initial active centers, but also to the radiative decomposition, which causes a degenerate ramification. Further research is needed for the problem of whether the decomposition of peroxides and aldehydes is due to direct absorption of radiation energy only, or whether the energy may be transferred their molecules by collision with ions or excited nitrogen molecules. The kinetic phenomena observed are assumed to be related to a direct or indirect effect of radiation on intermediate products. There are 6 figures.

ASSOCIATION: Fiziko-khimicheskiy institut imeni L. Ya. Karpova, Moskva (Physicochemical Scientific Institute imeni L. Ya. Karpov, Moscow)

SUBMITTED: September 13, 1960

Card 3/3

S/190/63/005/001/010/020
B101/B186

AUTHORS: Milinchuk, V. K., Pshezhetskiy, S. Ya., Kotov, A. G., Tupikov, V. I., Tsivenko, V. I.

TITLE: Formation and recombination of free radicals by gamma-irradiation of polypropylene. I

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 5, no. 1, 1963, 71-74

TEXT: The effect produced by the amorphous and crystalline phases of irradiated polypropylene on the stabilization of free radicals was studied. The polypropylene was irradiated with Co^{60}, dose rate 700 rad/sec, and the nuclear magnetic resonance spectra were taken at -195 and +20°C. Conclusions: With a dose of 350 Mrad, the radical concentration in amorphous polypropylene was $\sim 2 \cdot 10^{20}$ radicals per g, which is twice as much as in crystalline polypropylene. At 20°C, however, the radical concentration in crystalline polypropylene was $\sim 5 \cdot 10^{18}$ radicals per g with a dose of 125 Mrad, which is one order of magnitude higher than in amorphous

polypropylene. Recombination in amorphous polypropylene irradiated at -195°C is faster than in crystalline polypropylene and is considerably accelerated, especially near the vitrification temperature. This is attributed to the fact that amorphous polypropylene at low temperatures promotes radical formation, whereas higher temperatures promote recombination. The e. p. r. spectra of crystalline polypropylene were found to change reversibly. The hyperfine structure of the e. p. r. spectrum taken at -195°C contained 9 lines, whereas at + 20°C 17 lines were found. There are 4 figures.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova
(Physicochemical Institute imeni L. Ya. Karpov)

SUBMITTED: July 17, 1961

S/844/62/000/000/001/129
D290/D307

AUTHORS: Pshezhetskiy, S. Ya. and Tal'roze, V. L.

TITLE: The elementary processes of radiation chemistry and the mechanisms of various radiation-chemical reactions

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 5-27

TEXT: The authors review the elementary processes occurring when electrons interact with molecules and discuss the mechanisms of some of the subsequent reactions. They discuss the subject under the following main headings: 1. Fundamental primary processes of radiation chemistry; 2. Fundamental secondary elementary processes of radiation chemistry; 3. The elementary processes of radiation chemistry in condensed phases; 4. Fundamental types of complex radiation-chemical reactions and the mechanisms of some of these reactions. The authors conclude that more use must be made of physical methods which give direct information about the fundamental

Card 1/2

The elementary processes ... S/844/62/000/000/001/129
D290/D307

primary processes of radiation chemistry. There are 5 figures.

ASSOCIATION: Institut khimicheskoy fiziki AN SSSR; Fiziko-khimicheskiy institut im. L. Ya. Karpova (Institute of Chemical Physics AS USSR; Physico-Chemical Institute im. L. Ya. Karpov)

Card 2/2

KOTOV, A.G.; PSHEZHETSKIY, S.Ya.; MILINCHUK, V.I.; TUPIKOV, V.I.; TSIVENKO, V.I.

Formation and recombination of radicals by γ-irradiation of frozen H_2O_2 - H_2O solutions. Kin. i kat. 4 no.6:926-929 N-D '63. (MIRA 17:1)

1. Fiziko-khimicheskiy institut imeni Karpova.

L 12431-63 EPR/EWP(j)/EPF(c)/EWT(1)/EWT(m)/BDS AFFTC/ASD Ps-4/
Pc-4/Pr-4 RM/WW
ACCESSION NR: AP3001171 S/0190/63/005/006/0946/0946 82

AUTHOR: Milinchuk, V. K.; Pshezhetskiy, S. Ya.

TITLE: The action of light on free radicals in gamma-irradiated polymers

SOURCE: Vy*sokomolekulyarny*ye soyedineniya, v. 5, no. 6, 1963, 946

TOPIC TAGS: ultraviolet light, irradiation, gamma-rays, polymers, free radicals

ABSTRACT: The polymers under study were subjected at various temperatures to gamma-irradiation by Co sup 60 in a vacuum up to 5x10 sup -5 mm mercury and subsequently treated at 77C K with ultraviolet light. The polymers containing ultraviolet-absorbing groups at a range of 2500-3500 Angstrom, such as polyvinyl alcohol, polyvinylacetate, polymethylmethacrylate, polycaprolactam, polystyrene, and polybutadiene, showed a loss of radicals. This was accompanied by a modified appearance of the electron paramagnetic resonance spectrum, as well as by a modified spectrum without a lowering in the number of radicals. As to polymers which do not possess ultraviolet-light-absorbing groups, such as polyethylene, polypropylene, and polymethylsiloxane, irradiation does not cause here destruction of radicals. The mechanism causing the destruction and transformation of radicals by ultraviolet light is presumably linked to the migration of energy from the receptor

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L 12431-63
ACCESSION NR: AP3001171

groups, and thence along the polymeric chain towards the free radical. The absorbed energy may facilitate the migration of a free valency by lowering the barrier potential for the migration of hydrogen atoms, thus causing a recombination of free radicals with the formation of double bonds or links. Orig. art. has: 1 figure. The paper is a letter to the editor.

ASSOCIATION: none

SUBMITTED: 25Dec62 DATE ACQ: 01Jul63 ENCL: 00

SUB CODE: 00 NO REF SOV: 000 OTHER: 000

Card 2/2

TUPIKOV, V.I.; TSIVENKO, V.I.; PSHEZHETSKIY, S.Ya.; KOTOV, A.G.; MILINCHUK, V.K.

Formation and recombination of radicals in the γ-irradiation of solid ammonia and hydrazine. Zhur.fiz.khim. 37 no.1:138-142 Ja '63. (MIRA 17:3)

1. Fiziko-khimicheskiy institut imeni Karpova.

L 17711-63 EWP(j)/EPF(c)/EWP(q)/EWT(m)/BDS AFFTC Pc-4/Pr-4
RM/WW/JD

ACCESSION NR: AP3004063 S/0076/63/037/007/1549/1556

AUTHORS: Slavinskaya, N. A.; Gribova, Ye. I.; Demidova, G. G.; Kamenetskaya, S. A.; Pshezhetskiy, S. Ya.

TITLE: Effect of ozone on the kinetics of butane oxidation

SOURCE: Zhurnal fizicheskoy khimii, v. 37, no. 7, 1963, 1549-1556

TOPIC TAGS: ozone, butane, oxygen

ABSTRACT: The effect of ozone on the kinetics of butane oxidation with oxygen has been investigated. In a previous experiment, an investigation was made of the effect of ozone on the critical ignition point of some hydrocarbons. Ozone accelerates the reaction, shortens the induction period, lowers the effective activation energy, and increases chain branching. The effect of ozone is mainly associated with the facilitation of the generation of the initial active centers. Its effect on the butane oxidation kinetics is in agreement with the experimental data obtained previously with the ignition of butane-oxygen mixtures. During the oxidation of butane with ozone at an elevated temperature, the main reaction is the decomposition of ozone and the reaction of butane with the atomic oxygen resulting from the above decomposition: $C_4H_{10}+O_3 \rightarrow C_4H_9O+H_2O$. Orig. art. has:

Card 1/2

L 17711-63

ACCESSION NR: AP3004063

13 figures, 2 tables and 8 formulas.

ASSOCIATION: Fiziko-khimicheskiy institut im. P. Ya. Karpova (Physicochemical institute)

SUBMITTED: 21Jul62 DATE ACQ: 15Aug63 ENCL: 00

SUB CODE: CH NO REF SOV: 010 OTHER: 004

Card 2/2

L 15778-63 EPR/EPF(c)/EWP(q)/EWT(m)/BDS AFFTC/ASD Ps-4/Pr-4
BW/RM/WW/JD/JW/JFW

ACCESSION NR: AP3004986 S/0076/63/037/008/1871/1875

AUTHOR: Sorokin, Yu. A.; Tsivenko, V. I.; Pshezhetskiy, S. Ya.

TITLE: Hydrazine formation on γ-irradiation of liquid ammonia and of an aqueous ammonia solution

SOURCE: Zhurnal fiz. khimii, v. 37, no. 8, 1963, 1871-1875

TOPIC TAGS: hydrazine, hydrazine formation, nitrogen, hydrogen, gamma induced radiolysis, gamma radiation, radiolysis, ammonia, liquid ammonia, ionic mechanism, aqueous ammonia solution, ammonia decomposition, hydrazine decomposition, decomposition, free radical mechanism

ABSTRACT: The formation of hydrazine in the gamma-ray-induced radiolysis of liquid ammonia and frozen aqueous ammonia at various temperatures has been studied, and possible mechanisms for the reactions have been corsidered. The product yields expressed as mols formed per 100 ev of energy absorbed were determined, and the temperature dependence of the yields was studied at -70, -26, and +15C for liquid ammonia, -195C for solid ammonia, and -195C for frozen

Card 1/4

ACCESSION NR: AP3004986

aqueous ammonia in various concentrations. A Co^{60} source for gamma-irradiation of a sample in a glass ampule capable of withstanding high pressures was used. After evaporation of the ammonia, the hydrazine formed was determined colorimetrically by the color reaction of p-(dimethylamino)benzaldehyde in aqueous solution. For the radiolysis of liquid ammonia with doses on the order of 10^{21} ev/g NH_3, at a dose rate of 2×10^{16} ev/g NH_3·sec, a linear relationship was obtained between hydrazine, hydrogen, and nitrogen concentration and absorbed dose at -70, -26, and +15C. It was found that the yields of N_2 and H_2 were virtually independent of temperature. The yield of hydrazine decreased with an increase in temperature. For example, with an increase from -70 to 15C, the hydrazine yield dropped from 0.18 to 0.01 mol/100 ev, the nitrogen yield rose from 0.12 to 0.21 mol/100 ev, and the hydrogen yield remained at 0.64—0.68 mol/100 ev. Therefore, the nitrogen-yield increase can be attributed to an increase in the decomposition of hydrazine. The decrease in hydrazine yield with an increase in temperature may be due in part to the temperature dependence of the reaction

$$\dot{N}H_2 + N_2H_4 \rightarrow NH_3 + \dot{N}_2H_3, \quad (1)$$

ACCESSION NR: AP3004986

and in part to an increase in the diffusion rate of $\dot{N}H_2$ radicals from tracks, which prevents their recombination in the tracks to form hydrazine and favors reaction (1) in the "bulk" of the liquid ammonia. In the radiolysis of solid ammonia at -195C, a linear relationship was also obtained between hydrazine concentration and absorbed dose, corresponding to the mechanism of hydrazine formation by recombination of $\dot{N}H_2$ radicals. On an increase in temperature, trapped $\dot{N}H_2$ radicals recombine to form hydrazine. For the radiolysis of the frozen aqueous ammonia solution, the plot of hydrazine concentration versus initial percent NH_3 was characterized by a maximum at 50%, which suggests that water participated in the formation of hydrazine. To explain this participation, a free-radical and an ionic mechanism were proposed. The free-radical mechanism is described by the following reactions, which occur on irradiation:

$$\dot{O}H + NH_3 \rightarrow H_2O + \dot{N}H_2, \quad (2)$$

$$\dot{H} + NH_3 \rightarrow H_2 + \dot{N}H_2, \quad (3)$$

$$H_2O^+ + NH_3 \rightarrow H_3O^+ + \dot{N}H_2. \quad (4)$$

L 15778-63

ACCESSION NR: AP3004986

The ionic mechanism is described by the reactions:

$$NH_4^+ + e(aq) \rightarrow NH_3 + H, \quad (5)$$

$$NH_4^+ + e(aq) \rightarrow \dot{N}H_2 + H_2, \quad (6)$$

$$NH_3^+ + OH^- \rightarrow \dot{N}H_2 + H_2O, \quad (7)$$

$$NH_3^+ + e(aq) \rightarrow \dot{N}H_2 + H. \quad (8)$$

The final step of the reactions is the formation of hydrazine by recombination of the $\dot{N}H_2$ radicals on heating. Orig. art. has: 5 figures, 14 formulas, and 1 table.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Scientific Research Institute)

SUBMITTED: 28Oct62 DATE ACQ: 06Sep63 ENCL: 00

SUB CODE: CH NO REF SOV: 004 OTHER: 001

Card 4/4

L 18303-63 EPR/EPF(c)/EWP(q)/EWT(m)/BDS AFFTC/ASD Ps-4/Pr-4
WW/JW/JFW/JD

ACCESSION NR: AP3004990 S/0076/63/037/008/1900/1903 72

71

AUTHORS: Tupikov, V. I.; Pshezhetskiy, S. Ya.

TITLE: Formation and reaction of free radicals in solid ammonia and hydrazine, formed by Gamma-irradiation

11 27 11 27

SOURCE: Zhurnal fiz. khimii, v. 37, no. 8, 1963, 1900-1903

TOPIC TAGS: Gamma-irradiation, EPR, ammonia

ABSTRACT: The presence of reaction of $\dot{N}H_2$ radicals with NH_3 molecules, and the recombination of NH_2 radicals with solid Gamma-irradiated NH_3 was established by electron paramagnetic resonance. Results showed that the mechanism of radical recombination is the migration of free valences and H atoms. The mechanism can cause the phenomenon of formation of high concentrations of radicals by irradiating solid materials. The recombination of $\dot{N}H_2$ and $\dot{N}_2H_3$ radicals with NH_3 and N_2H_4 under influence of ultraviolet irradiation was established. The reaction of $\dot{O}H$ radicals with NH_3 molecules at liquid nitrogen temperature under influence of uv was discovered; $\dot{N}H_2$ and $\dot{H}O_2$ radicals are formed by the reaction. Orig. art. has: 4 figures, 1 table, 7 equations.

ASSN: Physicochemical scientific research institute.

Card 1/2

MILINCHUK, V.K.; PSHEZHETSKIY, S.Ya.

Effect of ultraviolet light on free radicals in γ-rayed polypropylene. Dokl. AN SSSR 152 no.3:665-667 S '63. (MIRA 16:12)

1. Fiziko-khimicheskiy institut im. L.Ya.Karpova. Predstavleno akademikom S.S.Medvedevym.

L 27864-65 EWG(j)/EWT(m)/EPF(c)/EPF(n)-2/EPR/EWP(j)/T/EWP(t)/EWP(b)/EWA(h)/EWA(l) Pc-4/Pr-4/Ps-4/Peb/Pu-4 IJP(c) JD/GG/GS/RM

ACCESSION NR: AT4049842 S/0000/64/000/000/0064/0069

AUTHOR: Milinchuk, V. K.; Pshezhetskiy, S. Ya.

TITLE: Formation and recombination of radicals during gamma-irradiation of polyvinyl alcohol and the solid solution of hydrazine in polyvinyl alcohol

SOURCE: Khimicheskiye svoystva i modifikatsiya polimerov (Chemical properties and the modification of polymers); sbornik statey. Moscow, Izd-vo Nauka, 1964, 64-69

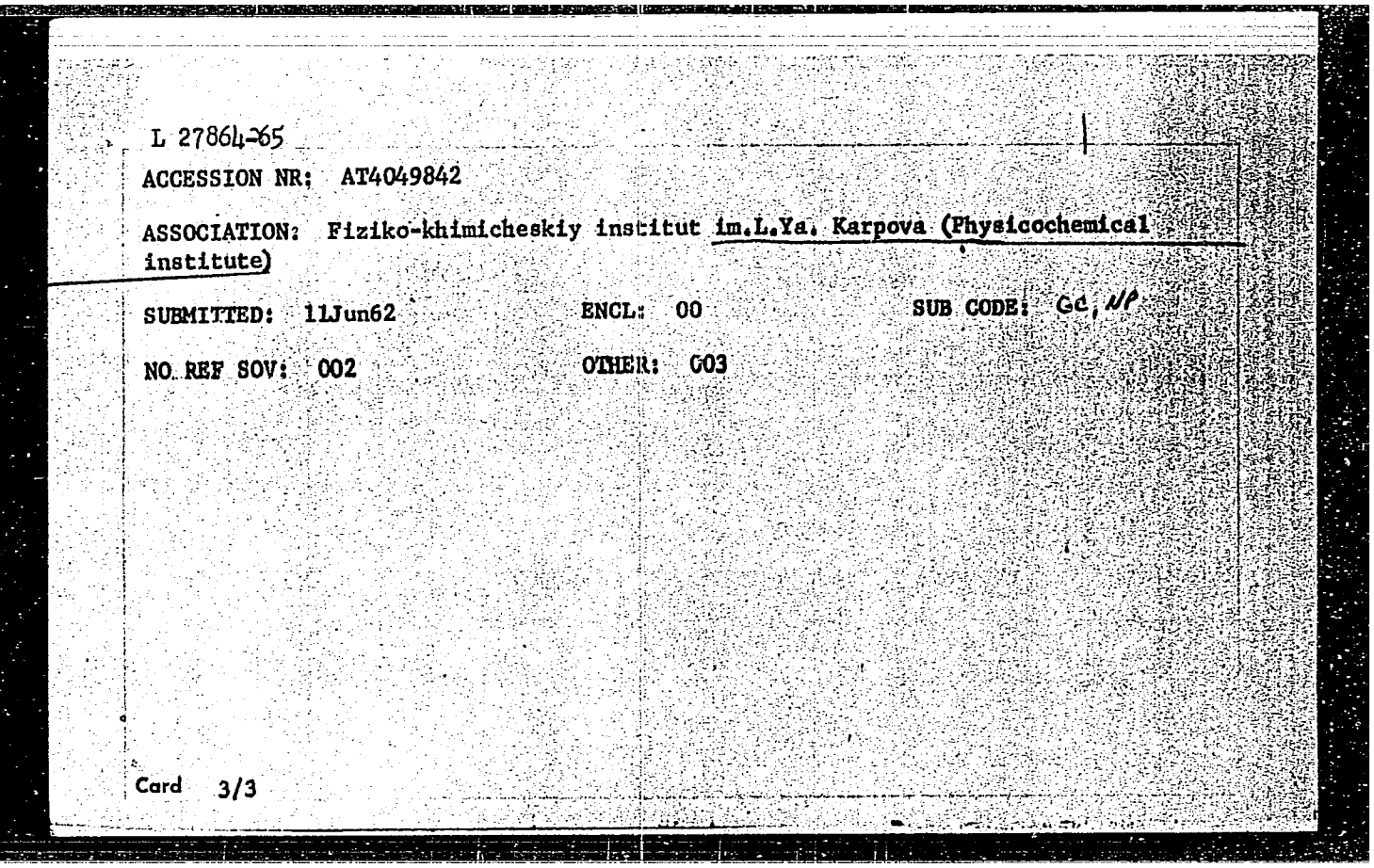
TOPIC TAGS: polyvinyl alcohol, solid solution, hydrazine, gamma-irradiation, electron paramagnetic resonance

ABSTRACT: In experiments on frozen hydrazine, its solid solution in polyvinyl alcohol and pure polyvinyl alcohol, it was established that the electron paramagnetic resonance (EPR) signal during irradiation of hydrazine is a single line. The most probable radical formed is N_2H_3. The measurements were made on films consisting of 30% hydrazine and 70% polyvinyl alcohol (with Co^{60} as source of γ-irradiation and a dose of 600 Mrad/sec at 77K or at room temperature). The irradiated samples were kept in liquid nitrogen. The EPR spectrum of this mixture shows an overlap of the EPR signals from hydrazine and pure polyvinyl alcohol. The difference in the spectra depending on the temperature of irradiation

Card 1/3

is discussed. The relationship between the concentration of radicals and the irradiation dose is plotted. The number of radicals in the solution at 77K increases with increasing irradiation dose, with a linear relationship between them up to about 15 Mrad. The accumulation of radicals depends on the temperature of irradiation for both crystalline and amorphous polymers. At room temperature in the solid solution, the radicals recombine more easily than in pure polyvinyl alcohol. The temperature effect is apparently due to the different mechanisms of recombination and formation of radicals at these temperatures. In the solid solution, recombination begins below 180K, then increases rapidly over the range of 193-203K. The relative concentration of radicals plotted against time for pure polyvinyl alcohol and the solid solution at 258-290K shows that, with time, the concentration tends not to a zero value but to a certain value which can be considered as a constant for the given temperature. The activation energy of recombination was determined by the given equation for polyvinyl alcohol (273-290K) as 10 ±2 kcal/mole; for the solid solution at 183-193K ... was the same. It was established that the polymeric polyvinyl alcohol matrix in ...rferes with the recombination of radicals formed from hydrazine to a greater e...ent than the actual molecular network of hydrazine. The kinetics of the recomb...ation of radicals in the solid solution and in pure polyvinyl alcohol follow an e...ation of the second order. Orig. art. has: 5 figures and 2 formulas.

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343510012-1"



L 27864-65

ACCESSION NR: AT4049842

ASSOCIATION: Fiziko-khimicheskiy institut im.L.Ya. Karpova (Physicochemical institute)

SUBMITTED: 11Jun62 ENCL: 00 SUB CODE: GC, NP

NO. REF SOV: 002 OTHER: 003

Card 3/3

L 19611-65 EWG(j)/EWT(m)/EPF(c)/EPF(n)-2/EWP(j)/T/EWA(h)/EWA(1) Pc-4/Pr-4/Pu-4/Peb RPL/AFWL/AS(mp)-2/SSD/ASD(a)-5/RAEM(c)/SSD(c)/RAEM(i)/ESD(gs)/ESD(t)
ACCESSION NR: AT4049861 GG/RM/WW/JFW/MLK S/0000/64/000/000/0222/0227

AUTHOR: Milinchuk, V.K., Pshezhetskiy, S. Ya.

TITLE: Recombination and conversion of free radicals in certain Gamma irradiated polymers during heating and exposure to ultraviolet

SOURCE: Khimicheskiye svoystva i modifikatsiya polimerov (Chemical properties and the modification of polymers); sbornik statey. Moscow, Izd-vo Nauka, 1964, 222-227

TOPIC TAGS: free radical, heated polymer, ultraviolet light, polypropylene, polyvinyl alcohol, polyvinyl acetate, Gamma radiation, electron paramagnetic resonance

ABSTRACT: The authors used the method of electron paramagnetic resonance (EPR) to study the recombination processes of free radicals in δ-irradiated polypropylene, polyvinyl alcohol and polyvinyl acetate during heating and under the influence of ultraviolet light at the temperature of liquid nitrogen. Weighed samples were placed in quartz ampoules and evacuated to a residual pressure of $\sim 10^{-5}$ mm Hg. The sealed ampoules, immersed in liquid nitrogen, were δ-irradiated (Co^{60}) at an intensity of $\sim$ 560 rad/sec. EPR spectra were recorded on a RE 1301 radiospectrometer. The number of free radicals in irradiated samples was determined by comparing their signal with a standard signal from a single crystal of the paramagnetic salt $CuCl_2 \cdot$

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L 19611-65
ACCESSION NR: AT4049861

2

$2H_2O$). During the heating of the γ-irradiated polypropylene, the initially formed alkyl radicals are converted into radicals that are localized at the double and conjugated bonds. In the case of polyvinyl acetate and polyvinyl alcohol, there is recombination of radicals at the temperature of liquid nitrogen under the influence of ultraviolet light; this may be connected with the excitation of macromolecules. It is concluded that at low temperatures the recombination of radicals is possible in accordance with the mechanism of the migration of free valences along the polymer chain. Orig. art. has: 3 figures and 3 structural formulas.

ASSOCIATION: Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (Physico-Chemical Scientific Research Institute)

SUBMITTED: 19Jan63 ENCL: 00 SUB CODE: OC, MT

NO REF SOV: 009 OTHER: 007

Card 2/2

ACCESSION NR: AP4032567 S/0190/64/006/004/0666/0671

AUTHORS: Milinchuk, V. K.; Pshezhetskiy, S. Ya.

TITLE: EPR study of free radical conversion kinetics in gamma-irradiated polypropylene

SOURCE: Vy*sokomolek. soyedin., v. 6, no. 4, 1964, 666-671

TOPIC TAGS: crystalline polypropylene, hyperfine structure, alkyl radical, polyene radical, conversion kinetics, polymer, free valence migration, macromolecule

ABSTRACT: A kinetic analysis was made of the hyperfine structure of EPR spectra in crystalline polypropylene to determine the conversion of alkyl(I) radicals into alkyl(II) and polyene(III) radicals. The I to II to III conversion is characterized by the ratios of the EPR spectral components $\beta_1 = h_1/h_2$, $\beta_2 = h_1/h_3$ in turn characterizing the radical concentration ratios II:I and III:I. The conversion kinetics was carried out by γ - irradiating the polymer at 77K with 500, 1000 and 1500 Mrad radiation dose, heating at various temperatures (273K to 323K) for several minutes, and subsequently immersion in liquid nitrogen, at which point the EPR

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ACCESSION NR: AP4032567

spectra were recorded. The results confirm the possibility of such a radical conversion by means of a possible mechanism of free valence migration in the macromolecule. An expression is derived for the radical conversion rate β_1 given by

$$\beta_1 = \frac{[R_2]}{[R_0]} = \frac{kt}{(1/[R_0]) + kt}.$$

This gives a magnitude close to the recombination rate constant of polypropylene radical. The activation energy of radical I to radical II conversion is estimated to be 6 ± 1 kcal/mol. Orig. art. has: 13 formulas and 3 figures.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Institute of Physical Chemistry)

SUBMITTED: 24Apr63 ENCL: 00

SUB CODE: OC NO REF SOV: 003 OTHER: 002

Card 2/2

L 10826-65 EWG(j)/EWT(m)/EPF(c)/EPF(n)-2/EPR/EWP(j)/T/EWA(h)/EWA(l) Pc-4/
Pr-4/Ps-4/Pu-4/Peb EPL GG/RM/WW/JFW

ACCESSION NR: AP4045426 S/0190/64/006/009/1605/1611

AUTHOR: Milinchuk, V. K.; Pshezhetskiy, S. Ya.

TITLE: Effect of light on free radicals stabilized in gamma-irradiated polyvinylacetate and polymethylmethacrylate

SOURCE: Vy*sokomolekulyarny*ye soyedineniya, v. 6, no. 9, 1964, 1605-1611

TOPIC TAGS: poly[vinylacetate], poly[methylmethacrylate], polymer spectrum, EPR spectrum, free radical, polymer structure, irradiated polymer

ABSTRACT: The authors have extended their spectral studies of gamma-irradiated polymers to the investigation of the electronparamagnetic resonance (EPR) spectra of gamma-irradiated polyvinylacetate and polymethylmethacrylate under the influence of ultraviolet and visible light. Discussing the study, in which the polymers were gamma-irradiated at 77K and an RE1301 radiospectrometer was used, the authors without further details of the procedure, give the following results: a) the EPR spectrum consists of three well-resolved superfine structural components; red (KS-10 filter) and yellow (ZhS-12 filter) light destroy the free radicals without appreciably affecting the spectrum pattern; $\lambda \leqslant 3800$A and UV light markedly affect the spectrum pattern (see Fig. 1 of the Enclosure); b) the superfine structure is poorly resolved, showing, in a carefully recorded spectrum, eleven weakly

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L 10826-65
ACCESSION NR: AP4045426

resolved lines; visible light tends to intensify the lines and change the spectrum pattern (Fig. 2 of the Enclosure); the free radicals appear to be unaffected by visible light and insignificantly affected by UV light; heating from 77 to 204K changes the spectrum pattern and decreases the concentration of free radicals. The authors conclude that: 1) free radical phototransformations are responsible for the spectral changes, 2) light-induced stabilized radical transformations are reversible and the initial pattern of an EPR spectrum can be restored by sufficiently protracted exposure to 77K, and 3) there exists a dynamic equilibrium between the isomeric modifications of free radicals. Possible radical structures are suggested and the mechanism of the reversible transformations is discussed. Orig. art. has: 6 figures and 9 chemical equations.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physical-Chemical Institute)

SUBMITTED: 17Oct63 ENCL: 02 SUB CODE: OC

NO REF SOV: 005 OTHER: 006

Card 2/4

L 10826-65
ACCESSION NR: AP4045426

ENCLOSURE: 01

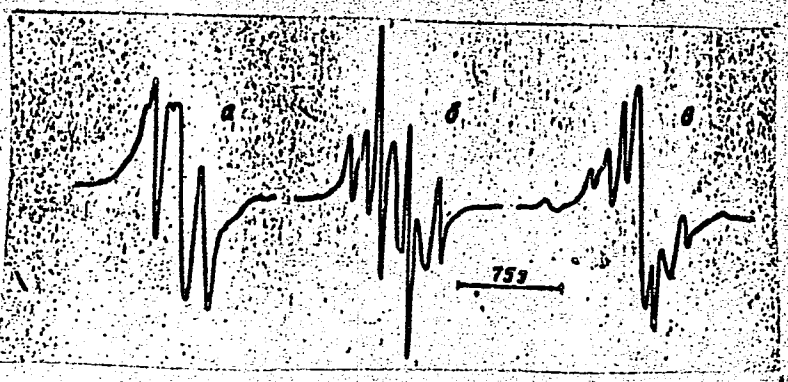

Fig. 1. a - EPR spectrum for polyvinylacetate, gamma-irradiated at 77K; b - spectrum of the same polymer sample, irradiated with visible light (SZS-22 filter) at 77K; c - irradiated with UV light (UFS-1 filter) at 77K. Measuring temperature 77K.

Card 3/4

L 10826-65
ACCESSION NR: AP4045426

ENCLOSURE: 02

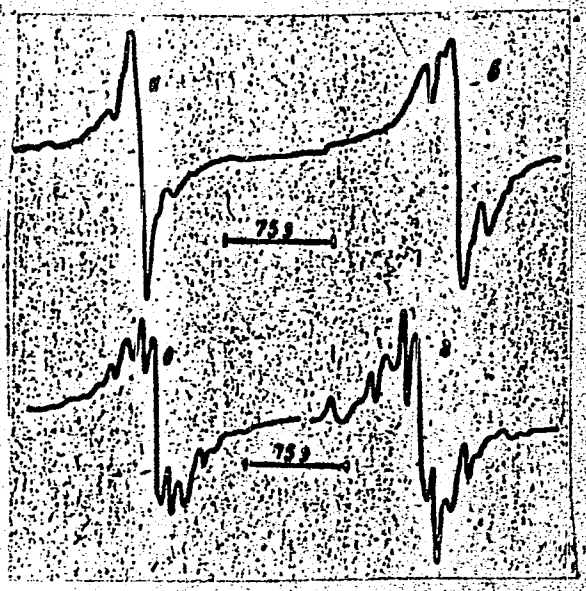

Fig. 2. a - EPR spectrum for polymethylmethacrylate, gamma-irradiated at 77K; b - spectrum of the same sample, irradiated through a ZhS-12 filter; c - ditto through a SZS-22 filter; d - ditto through a FS-6 filter. Measured in liquid nitrogen.

Card 4/4

SOROKIN, Yu.A.; FSHENICHETSKIY, S.Ya.

Decomposition of ammonia by γ-rays. Zhur. fiz. khim. 38 no.3: 798-801 Mr '64. (MIRA 17:7)

1. Nauchno-issledovatel'skiy fiziko-khimicheskiy institut imeni L. Ya. Karpova.

L 34705-65 EPF(c)/EPF(n)-2/EWA(h)/EWP(j)/EWT(m)/EWA(l) Pc-4/Pr-4/Pu-4/Peb
ACCESSION NR: AP4044435 RPL GG/RM S/0076/64/038/008/1920/1925

AUTHOR: Kotov, A. G.; Pshezhetskiy, S. Ya.

TITLE: EPR study of the formation of free radicals upon γ-irradiation of certain ammonium and hydrazonium salts

SOURCE: Zhurnal fizicheskoy khimii, v. 38, no. 8, 1964, 1920-1925

TOPIC TAGS: electron paramagnetic resonance, free radical, hydrozonium sulfate, hydrazonium chloride, ammonium chloride, gamma irradiation

ABSTRACT: The article describes the investigation of EPR spectra of γ-irradiated NH_4Cl, $N_2H_4 \cdot HCl$ and $H_2H_4 \cdot H_2SO_4$ which characterize the nature of the produced radicals. It was found that formation of ion-radicals during irradiation of ammonium and hydrazonium salts occurs in the same manner as during irradiation of solid ammonia and hydrazine, i.e., due to splitting of hydrogen atoms. The produced ion-radicals NH_3^+ and $N_2H_4^+$ are stabilized by the coulomb's field of the ionic lattice. In γ-irradiated hydrazonium chloride atomic hydrogen spect-

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L 34705-65

ACCESSION NR: AP4044435

rum was observed and the change of the concentration of ion-radicals was not observed upon its disappearance. It is believed, therefore, that the processes $N_2H_5^+ + H = N_2H_4^+ + H_2$; $N_2H_4^+ + H = N_2H_5^+$; are not very probable in the stabilization of atomic hydrogen. The EPR spectra of γ-irradiated salts change during heating and are dependent on the temperature of measurement, which explains the anisotropy of the hyperfine splitting due to excitation of the rotational and vibrational degrees of freedom. It was shown that during irradiation of ammonium chloride or solid ammonia NH_3^+ is converted to $N_2H_4^+$ ion-radical. Orig. art. has: 3 figures

ASSOCIATION: Fiziko-khimicheskiy institute im. P. Ya. Karpova (Physical Chemistry Institute)

SUBMITTED: 28Jun63 ENCL: 00

SUB CODE: GP, GC NO REF SOV: 002 OTHER: 005

Card 2/2

L 21332-65 EWT(m)/EPF(c)/EWP(j)/ Pc-4/Pr-4 ASD(a)-5/AFWL/SSD/AS(mp)-2/
RAEM(c)/RAEM(i)/ESD(ge)/ESD(t)/RPL WW/JFW/RM

ACCESSION NR: AP4044436 S/0076/64/038/008/1926/1930

AUTHOR: Kotov, A. G. (Moscow); Pshezhetskiy, S. Ya. (Moscow)

B

TITLE: EPR study of the annihilation processes of ion-radicals in ionic crystals

SOURCE: Zhurnal fizicheskoy khimii, v. 38, no. 8, 1964, 1926-1930

TOPIC TAGS: free radical annihilation, electron paramagnetic resonance, color center, EPR spectrum

ABSTRACT: It was shown that upon gamma irradiation of NH_4Cl, $N_2H_4.HCl$ and $N_2H_4.H_2SO_4$ one obtains NH_3^+ and $N_2H_4^+$ ion-radicals. The coulombic repulsion of ion-radicals and their low mobility in ionic crystals at moderate temperatures give reasons to believe that annihilation of ion-radicals as a result of motion is improbable. The annihilation mechanism of ion-radicals in this case is a more complex process which occurs under conditions of stationary ion-radicals in crystal lattice nodes. This article presents data which enable one to make some conclusions regarding the mechanism of annihilation of ion-radicals in some ionic

L 21332-65

ACCESSION NR: AP4044436

crystals. The study was carried out on the change of concentration of ion-radicals in NH_2Cl, $N_2H_4 \cdot HCl$ and $N_2H_4 \cdot H_2SO_4$ upon change of temperature and time of heating and upon illumination with visible light and ultraviolet light. These salts were previously irradiated by Co^{60} gamma source at liquid nitrogen temperature. The concentration of ion-radicals was determined by comparing the area of EPR spectrum with the spectrum of standard $CuCl_2 \cdot 2H_2O$ paramagnetic crystal. It was found that upon heating NH_3^+ and $N_2H_4^+$ ion-radicals are annihilated in the same temperature interval as the color centers. In NH_4Cl change of concentration of NH_3^+ is observed upon irradiation with ultraviolet and visible light. The rate constant for the disappearance of ion-radicals is a function of temperature. In colorless salt $N_2H_4 \cdot HCl$, $N_2H_4^+$ ion radicals vanish at higher temperature. The annihilation of ion radicals occurs during their recombination with electrons of color centers. Orig. art. has: 4 figures

ASSOCIATION: None

SUBMITTED: 00 ENCL: 00 SUB CODE: GC, NP

NR REF SOV: 004 OTHER: 005

Card 2/2

L 23054-65 EWG(j)/EWT(m)/EPF(c)/EPF(n)-2/EWP(j)/T/EWA(h)/EWA(1) Pc-4/
Pr-4/Pu-4/Peb RPL WW/JFW/GG/RM

ACCESSION NR: AP4047982 S/0076/64/038/010/2430/2436

AUTHOR: Tupikov, V. I. (Moscow); Pshezhetskiy, S. Ya. (Moscow)

TITLE: Investigation of radicals formed by γ-irradiation of trioxane

SOURCE: Zhurnal fizicheskoy khimii, v. 38, no. 10, 1964, 2430-2436

TOPIC TAGS: trioxane, gamma irradiation, radical formation, EPR spectrum, trioxane chain postpolymerization

ABSTRACT: In order to explain the nature of the active centers in irradiated trioxane an EPR study was made of the radicals formed upon γ-irradiation of a trioxane monocrystal at -196 C, and of the behavior of these radicals at different temperatures. Molecular ion radicals, the biradicals $O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}CH_3$, and radicals generated by the dissociation of the C-H bond--paramagnetic structures giving a weakly split singlet, were formed. Formyl HCO radicals, resulting from the rupture of the trioxane ring, were also formed. On heating the γ-irradiated trioxane crystals to -70C the concentration of unpaired spins increased;

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L 23054-65

ACCESSION NR: AP4047982

2

this increase in radical concentration was attributed to the recombination of the ions with the electrons freed from the traps. Above -70 C this concentration started to decrease. The molecular ion radicals and the radicals characterized by weak splitting of the singlet were retained on heating to +50 C; the initiation of chain postpolymerization of trioxane may be attributed to this. Orig. art. has: 5 figures

ASSOCIATION:Nauchno-issledovatel'skiy fiziko-khimicheskiy institut im. L. Ya. Karpova (State-Scientific Physical-Chemical Institute)

SUBMITTED: 13Feb64 ENCL: 00

SUB CODE: GC, NP NO REF SOV: 002 OTHER: 005

Card2/2

L 23057-65 EWG(j)/EWT(m)/EPF(c)/EPF(n)-2/EPR/EWP(j)/EWP(b)/EWA(h)/EWA(l)
Pc-4/Pr-4/Ps-4/Pu-4/Peb RPL GG/RM/WW/JW/JFW/JD
ACCESSION NR: AP4047989 S/0076/64/038/010/2511/2513

AUTHOR: Tupikov, V. I.; Pshezhetskiy, S. Ya.

TITLE: Formation of free radicals by the γ-radiolysis of aqueous solutions of ammonia and hydrazine

SOURCE: Zhurnal fizicheskoy khimii, v. 38, no. 10, 1964, 2511-2513

TOPIC TAGS: ammonia, hydrazine, gamma radiolysis, free radical formation, EPR spectrum

ABSTRACT: The EPR spectra of frozen aqueous solutions of ammonia and hydrazine subjected to γ-radiation indicated that only the $\dot{N}H_2$ and $\dot{N}_2H_3$ radicals respectively, were formed. The radical yield depended on the composition of the solution and was maximum near the region of equimolecular composition. This was caused by the transfer of energy from the water molecule to the ammonia or hydrazine molecules (by not less than 10% of the activated water molecules), and by low temperature reaction of the OH radicals with ammonia and hydrazine. No

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L 23057-65
ACCESSION NR: AP4047989

$\dot{O}H$ or $H\dot{O}_2$ radicals were found, confirming hydrogen was split from the ammonia by the $\dot{O}H$ radical. Orig. art. has: 1 table and 2 figures.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physical-chemical Institute)

SUBMITTED: 24Feb64 ENCL: 00

SUB CODE: GC NO REF SOV: 004 OTHER: 001

Card 2/2

TUPIKOV, V. I.; PSHEZHETSKIY, S. Ya.

Free valence migration in stabilized olefin radicals under the effect of light. Dokl. AN SSSR 156 no. 1:114-117 My '64.
(MIRA 17:5)

1. Fiziko-khimicheskiy institut im. L. Ya. Karpova.
Predstavleno akademikom S. S. Medvedevym.

L 23342-65 EWT(m)/T DIAAP BW

ACCESSION NR: AP5002001 S/0020/64/159/006/1385/1388

AUTHOR: Sorokin, Yu. A.; Kotov, A. G.; Pshezhetskiy, S. Ya.;

TITLE: Study of radiolysis of ammonia adsorbed on surfaces of solids, by the method of electronic paramagnetic resonance

SOURCE: AN SSSR. Doklady, v. 159, no. 6, 1964, 1385-1388

TOPIC TAGS: ammonia radiolysis, matrix effect, electronic paramagnetic resonance, γ irradiation, radiolysis, cobalt 60

ABSTRACT: The effectiveness of utilization of the energy of nuclear radiation for chemical reactions is increased by the use of solid sorbents. However, the mechanism of the sensibilization is not clear. The authors investigated processes which take place on γ-irradiation of ammonia adsorbed in zeolite. Specimens of zeolite with adsorbed ammonia were irradiated with Co^{60} at the temperature of liquid nitrogen. The epr-spectrum were recorded. The spectrum of zeolite is a weakly anisotropic singlet. The spectrum of zeolite with adsorbed ammonia

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L 23342-65
ACCESSION NR: AP5002001

show a fine structure. With the increase of ammonia amount, this distortion is increased, and the original singlet disappears. The radical NH_2 in argon shows a different epr-spectrum (triplet) than in water and in zeolite. The differences could be explained by the effect of the matrix on the rotational degrees of freedom of NH_2. The formation of NH_2 apparently depends not only on the direct radiolysis, but also on the energy transfer from zeolite. Orig. art. has: 3 figures

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physical Chemical Institute)

SUBMITTED: 18Jul64 ENCL: 00 SUB CODE: GC, NP

NR REF SOV: 002 OTHER: 006

Card 2/2

L 55110-65 EWG(j)/EWT(m)/EWP(i)/EPF(c)/EPF(n)-2/EWG(m)/EWP(b)/EPR/EWP(e) Pr-4/
Ps-4/Pu-4 WW/DM/WH

ACCESSION NR: AP5014541 UR/0089/65/018/005/0492/0496 36 35

AUTHOR: Zhitneva, G. F.; Pshezhetskiy, S. Ya.; Slavinskaya, N. A.; Kamenetskaya, S. A.

TITLE: Reaction kinetics and the steady state in the system CO_2—CO—C under the influence of fast electrons

SOURCE: Atomnaya energiya, v. 18, no. 5, 1965, 492-496

TOPIC TAGS: carbon dioxide coolant, uranium graphite reactor, carbon dioxide reaction, reaction kinetics

ABSTRACT: The kinetics of the reaction between carbon dioxide and carbon under the influence of ionizing radiation is of interest in connection with the use of CO_2 as a reactor coolant. In view of the lack of adequate published data on this reaction, the authors present a report of a study on the kinetics and the general laws governing the establishment of the steady state in the system $CO_2 + C \rightarrow 2CO$. The radiation was simulated by fast electrons (200 keV) from an electron accelerator with an extracted beam. The temperature was varied from 25 to 400C, and the pressure from 200 to 600 mm Hg. The

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L 55110-65

ACCESSION NR: AP5014541

absorbed energy was 3.0×10^{15} eV/cm^{3}sec, and the current was 100 μA. The reaction vessel was heated electrically. The results show that the rate of the decomposition of CO_2 in the presence of carbon is independent of the concentration of CO_2, whereas the rate of decomposition of the CO is proportional to its concentration. The activation energy of both reactions is close to zero. The decomposition rate of both CO_2 and CO depends linearly on the intensity of radiation. The stationary concentration of CO which is established in the system after prolonged irradiation, does not depend on the intensity of radiation or on the temperature of the reaction zone, but depends on the surface of the carbon, as ascertained by tests with graphite bars and with powdered graphite. Orig. art. has: 8 figures, 4 formulas, and 4 tables. [02]

ASSOCIATION: None

SUBMITTED: 13May64 ENCL: 00 SUB CODE: NP

NO REF SOV: 000 OTHER: 002 ATD PRESS: 4024

Card 2/2

L 37696-65 EWG(j)/EWT(m)/EPF(c)/EPF(n)-2/EWP(j)/EWA(h)/EWA(l) Pc-4/Pr-4/
Peb/Pu-4 RPL GG/RM

ACCESSION NR: AP5006699 S/0076/65/039/002/0470/0472

AUTHOR: Roginskiy, V. A.; Kotov, A. G.; Pshezhetskiy, S. Ya.

TITLE: The effect of intermolecular compounds on the formation of radicals during gamma-irradiation of some solid binary solutions

SOURCE: Zhurnal fizicheskoy khimii, v. 39, no. 2, 1965, 470-472

TOPIC TAGS: Gamma irradiation, solid solution, binary solution, radical formation, intermolecular compound, free radical, electron paramagnetic resonance

ABSTRACT: The effects of intermolecular interaction in solid binary solutions under the influence of gamma-irradiation were studied experimentally. Three types of binary systems [illegible] at 77K from a Co-60 source: the ideal solutions $C_6H_5CH_3$ + n-C_6H_{14},

in the first and second types of systems [illegible] respectively, but it was markedly different from additive in the third type of solution,

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L 37696-65

ACCESSION NR: AP5006699

as shown in Fig. 1 of the Enclosure. The maximum deviation from additive behavior was found at component ratios corresponding to intermolecular association. The nitrogen compounds were shown to shield alcohol molecules from splitting. The shielding effect is caused by energy transfer from alcohol to nitrogen compounds. Thus, free radical formation increases if the N-H bonds are weaker than the C-H bonds in the alcohol (hydrazine-methanol system), and decreases if the N-H bonds are stronger (ammonia-methanol system). Orig. art. has: 4 figures and 1 formula.

ASSOCIATION: Fiziko-khimicheskiy institut im. L. Ya. Karpova (Physicochemical Institute)

SUBMITTED: 08Jan64 ENCL: 01 SUB CODE: OC, NP

NO REF SOV: 002 OTHER: 001

Card 2/3

L 17902-66 EWT(m)/EPF(c)/EPF(n)-2/EWP(j)/T/EWP(t)/EWP(b) IJP(c)/RPL JD/BW

ACCESSION NR: AP5021419 WW/JW/JG/JWD/WE/RM UR/0076/65/039/008/1955/1959 541.15

AUTHOR: Sorokin, Yu. A.; Pshezhetskiy, S. Ya.

TITLE: Kinetics and sensitization of the radiolysis of ammonia in the gas phase under the influence of fast electrons

SOURCE: Zhurnal fizicheskoy khimii, v. 39, no. 8, 1965, 1955-1959

TOPIC TAGS: ammonia radiolysis, hydrazine, rare gas, electron radiation, propylene

ABSTRACT: The kinetics of decomposition of ammonia and formation of hydrazine in the gas phase under the influence of fast electrons were investigated at room temperature. As the pressure rises, the reaction order changes from first to zero. The activation energy of the reaction is close to 1 kcal/mole. The kinetics of the reaction were interpreted with the aid of elementary processes involving the participation of NH_2 radicals. The sensitization of ammonia radiolysis by rare gases (Ne, Ar, Xe) and propylene was studied. Energy is transferred from the rare gases to ammonia with an 80% efficiency. Propylene in amounts of a few percent enhances the formation of hydrazine and depresses the reactions of decomposition of ammonia which

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